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Oxidation of sec-Alcohols with Ru(II)-Bearing Microgel Star Polymer Catalysts via Hydrogen Transfer Reaction: Unique Microgel-Core Catalysis

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Abstract

Oxidation of sec-alcohols was investigated with ruthenium-bearing microgel core star polymer catalysts [Ru(II)-Star]. The star polymer catalysts were directly prepared via $RuCl_2(PPh_3)_3$-catalyzed living radical polymerization of methyl methacrylate (MMA), followed by the arm-linking reaction with ethylene glycol dimethacrylate (**1**) in the presence of diphenylphosphinostyrene (**2**). Ru(II)-Star efficiently and homogeneously catalyzed the oxidation of 1-phenylethanol (**S1**) to give a corresponding ketone (acetophenone) in higher yield (92%) than analogues of polymer-supported ruthenium complexes. Importantly, the star catalyst afforded high recycling efficiency in the oxidation. They held catalytic activity against three times catalysis even though they were recovered under air-exposure every time, whereas the conventional $RuCl_2(PPh_3)_3$ lost the activity for same recycling procedure due to the deactivation by oxygen. The stability of the star catalyst during the recycle experiment was confirmed by detailed spectroscopic characterization. The star polymers also catalyzed oxidation of a wide range of sec-alcohols with aromatic and aliphatic groups. The substrate affinity was different from that of $RuCl_2(PPh_3)_3$, suggesting the unique selectivity caused by the specific structure.

Keywords

star polymers, ruthenium, metal-polymer complexes, oxidation, hydrogen transfer reaction, sec-alcohols

Introduction

The ultimate goal on catalyst design for chemical reactions would be the full compatibility between an efficient catalytic function and the practical availability. Homogeneous catalysts potentially can contribute to the improvement of activity due to numerous chances to encounter with substrates, however recovering from the products and their reuse have tended to be difficult. In contrast, insoluble (heterogeneous) supported catalysts[1b,1c,1e-1n] such as cross-linked polystyrene gel and silica-gel immobilized metal complexes have been developed to resolve such difficulties of removal and reuse for various organic reactions, although most of them are inferior to homogeneous ones regarding the activity. On the other hand, the recent advance of synthetic methodology for well-defined macromolecules has encouraged us to prepare homogeneous polymer (macromolecules)-supported catalysts[1a,1d,1e,1f,1l] providing both of catalytic functions and availability. More sophisticated design of the structure around catalytically active site would be responsible for advancement of catalytic functions.[2-7] Dendrimer-inside supported catalysts[2,3] are their typical representatives to give characteristic activity and selectivity due to the compartmentalized reaction space from outer environment.

Microgel-core star polymers[8-15] are quite intriguing as scaffolds to place catalysts,[12-15] because the star polymers carry a nano-size, compartmentalized, and cross-linked core in the center, from which lots of linear arms emanate. The polymer is fully soluble in various solvents dependent on the solubility of an arm polymer, thought the core is originally insoluble or hardly soluble due to the network structure. Motivated by these features, we have designed ruthenium-bearing microgel core star polymers[12] applicable to catalysis.[12a,12d] The star polymers were, in one-pot, synthesized by ruthenium [$RuCl_2(PPh_3)_3$]-catalyzed living radical

polymerization[16] of arm monomers, followed by the subsequent arm-linking reaction with a divinyl compound (**1**) in the presence of a phosphine ligand-bearing monomer (**2**)[12,17] (Scheme 1). The key is to employ the ligand monomers during the arm-linking process. Importantly, **2** induce the ligand exchange reaction with $RuCl_2(PPh_3)_3$, simultaneously the monomer copolymerized with **1** from an arm polymer. Thus, **2** efficiently entraps the ruthenium catalysts into the microgel core of the resulting star polymers [Ru(II)-Star]. The obtained Ru(II)-star polymers own lots of ruthenium complexes bound by phosphine ligand of the core that is compartmentalized from outer environments with plenty of arms. The high solubility of star polymers due to soluble arms and the steady encapsulation of ruthenium complexes into the core would be compatible with high activity in catalysis and high stability realizing catalyst recycles.[12d]

Scheme 1

Herein, we investigated the ruthenium-bearing microgel star polymers [Ru(II)-Star] as catalysts for the oxidation of sec-alcohols coupled with K_2CO_3 (base) and acetone (hydrogen acceptor) via hydrogen transfer reaction (Scheme 2).[12a,18-21] The catalytic performances were compared with the original $RuCl_2(PPh_3)_3$ and other types of supported catalysts. Effects of structures of star polymer catalysts on the catalytic activity were also examined, especially focused on the arm length, the core cross-linked amount, and the core-void volume. Discussion was focused on the unique activity, stability, and recyclability of the star catalysts in contrast to other types of supported catalysts and $RuCl_2(PPh_3)_3$.

Scheme 2

Experimental Section

Materials for the synthesis of polymer catalysts

Methyl methacrylate (TCI, purity>99%) was dried overnight over calcium chloride, and purified by double distillation from calcium hydride before use. $(MMA)_2$-Cl (Initiator) was prepared according to the literature.[22] Ethylene glycol dimethacrylate (**1**: Aldrich, purity >98%) was purified by distillation from calcium hydride before use. Diphenylphosphinostyrene (**2**) was kindly supplied by Hokko Chemical (purity >99%) or prepared according to the literature,[17a] and was degassed by reduced pressure before use. Polystyrene cross-linked with divinylbenzene, diphenylphosphinated (**3**: Aldrich; polystyrene cross-linked with 2% divinyl benzene; 3 mmol phosphine/g-resin) was degassed by reduced pressure before use. 2,2'-Azobis(isobutyronitrile) (Wako, purity >98%) was used as received. $RuCl_2(PPh_3)_3$ (Aldrich, 97%) was used as received and handled in a glove box under a moisture- and oxygen-free argon atmosphere (H_2O <1 ppm, O_2 <1 ppm). *n*-Bu_3N (TCI, purity >98%) was bubbled with dry nitrogen for more than 15 min immediately before use. Internal standards for gas chromatography (*n*-octane for MMA, tetralin for **1**) from dried overnight over calcium chloride, distilled twice from calcium hydride. Toluene (solvent) was purified by solvent dispensing system (HANSEN&CO., LTD.) before use. Hexane (Wako, dehydrated) was used as received. The solvents were bubbled with dry nitrogen for more than 15 min immediately before use.

Materials for the oxidation of sec-alcohols

The substrates [**S1**: 1-phenylethanol, TCI >98%; **S2**: 1-(4-chlorophenyl)ethanol, TCI >95%; **S3**: 1-hydroxyindan, TCI >99%; **S4**: cyclopentanol, Wako >99%; **S5**: cyclohexanol, Wako >98%; **S6**: 2-butanol, Wako >99%; **S7**: 2-octanol, Wako >98%] were degassed by reduced pressure or

bubbled with dry nitrogen for more than 15 min before use. K_2CO_3 (Wako, >99.5%) and acetone (Wako, dehydrated) were degassed by reduced pressure before use.

Characterization

The MWD curves, M_n, and M_w/M_n of the polymers were measured by size exclusion chromatography (SEC) in DMF containing 10 mM LiBr at 40 °C (flow rate: 1 mL/min) on three linear-type polystyrene gel columns (Shodex KF-805L; exclusion limit = 5 $\times 10^6$; pore size = 20-1000 A; 0.8 cm i.d.$\times$30 cm) that were connected to a Jasco PU-980 precision pump, a Jasco RI-930 refractive index detector, and a Jasco UV-970 UV/vis detector set at 270 nm. The columns were calibrated against 10 standard poly(MMA) samples (Polymer Laboratories; M_n = 1000–1200000; M_w/M_n = 1.06-1.22). ^{1}H NMR spectra were recorded in $CDCl_3$ at 25 °C on a JEOL JNM-LA500 spectrometer, operating at 500.16 MHz. The absolute weight-average molecular weight (M_w) of the polymers was determined by multi-angle laser light scattering coupled with SEC (SEC-MALLS) in DMF containing 10 mM LiBr at 40 °C on a Dawn E instrument (Wyatt Technology; Ga-As laser, λ = 690 nm). The refractive index increment (*dn/dc*) was measured in DMF at 40 °C on an Optilab DSP refractometer (Wyatt Technology; λ = 690 nm, c < 2.0 mg/mL). UV-vis spectra were analyzed in CH_2ClCH_2Cl at room temperature on Shimadzu MultiSpec 1500. The core-bound Ru(II) was calculated by using the absorbance at 475 nm and calibration plot made for $RuCl_2(PPh_3)_3$ (0.10-2.0 mM solution) at the same wavelength.

Synthesis of Ru(II)-Star (C1-C7)

The synthesis of star polymer catalysts (**C1-C7**) was carried out by the syringe technique under dry argon in baked flask equipped with a three-way stopcock.[12a,12b] Typically for **C2**, $RuCl_2(PPh_3)_3$ (0.20 mmol, 192 mg) was placed in a 50 mL round-bottomed flask. Then, toluene

(12.2 mL), *n*-octane (1.06 mL), *n*-Bu_3N (0.8 mmol, 2.0 mL of 400 mM toluene solution), MMA (40 mmol, 4.26 mL), and $(MMA)_2$-Cl (0.40 mmol, 0.48 mL of 839 mM toluene solution) were added sequentially in this order into the flask at 25 °C under dry argon. The total volume of the reaction mixture was thus 20.0 mL. After mixing, the solution was placed in an oil bath at 80 °C. After the polymerization had reached over ca.90% conversion in 48 h, **1** (4.0 mmol, 2.0 mL of 2000 mM toluene solution), **3** (1.0 mmol, 1.0 mL of 1000 mM toluene solution), tetralin (0.2 mL), $RuCl_2(PPh_3)_3$ (0.20 mmol, 192 mg), and toluene (6.8 mL) was added to the MMA prepolymer solution, and the further reaction proceeded. After 50 h, the reaction was terminated by cooling the mixture to -78 °C (conversion MMA/**1**/**2** = 98%/86%/100%; MMA and **1**: determined by gas chromatography; **2**: determined by ^{1}H NMR; star polymer yield = 82%: determined by SEC curves). The star polymers were precipitated into hexane under dry argon. The crude solid products were dissolved in toluene and purified by silica gel chromatography under argon to remove free ruthenium. The solution was evaporated under vacuum to give red-brown solid products (**C2**). SEC-MALLS (in DMF): $M_{w,star}$ = 390,000, 24 arms, R_g = 6.9 nm; UV-vis (CH_2ClCH_2Cl, r.t., 475 nm): 38 μmol Ru/g-polymer.

Synthesis of Ru(II)-Gel (C8)

In a 50 mL round-bottomed flask, $RuCl_2(PPh_3)_3$ (0.24 mmol, 230 mg) in toluene (24mL) was added into **3** (1.2 mmol phosphine, 0.4g) under dry nitrogen. The mixture was stirred at 80 °C for 28 h under dispersion to give red-brown Ru(II)-supported powder with colorless supernatant. The obtained powder was washed by toluene three times under dry argon. The supernatant exhibited no UV-vis absorption derived from $RuCl_2(PPh_3)_3$, indicating the quantitative introduction of Ru complexes into **3**. **C8**-bound Ru(II) = 420 μmol Ru/g-polymer: determined by UV-vis

analysis and the feed ratio of the ruthenium catalyst and **3**.

Synthesis of Ru(II)-Random (C9)

2,2'-azobis(isobutyronitrile) (0.3 mmol, 51.5 mg) was placed in a 50 mL round-bottomed flask. Then, toluene (4.08 mL), MMA (39.8 mmol, 4.24 mL), and **2** (2.09 mmol, 2.15 mL, 975 mM in toluene) were sequentially added in this order at 25 ^{o}C under dry argon. The mixture was placed in an oil bath at 80 ^{o}C for 25 h. The reaction was terminated by cooling the mixture to -78 ^{o}C, and the conversion of MMA and **2** was 99% and 100%, respectively. The obtained polymer was precipitated into hexane and filtered off, and dried under vacuum. The random phosphine-ligand polymer (**4**) had M_n of 16700, M_w/M_n of 2.24 by SEC and phosphine-ligand of 0.457 mmol/g-polymer calculated from the monomer conversion. In a 50 mL round-bottomed flask, $RuCl_2(PPh_3)_3$ (0.23 mmol, 217 mg) in toluene (23mL) was added into **4** (2.48 g, 1.13 mmol phosphine) under dry argon. The mixture was placed in an oil bath at 80 ^{o}C for 23 h. After the reaction was terminated by cooling to -78 ^{o}C, the solution was purified by silica gel chromatography (Wako Gel 200) under dry argon to remove free ruthenium. The polymer solution was evaporated under vacuum to give solid red-brown products (**C9**). SEC (DMF): M_n = 20700; M_w/M_n = 2.94; UV-vis (CH_2ClCH_2Cl, r.t., 475 nm): 50 μmol Ru/g-polymer.

Oxidation of sec-Alcohols Catalyzed by Ru(II)-Star (C2)

The typical procedure of Ru(II) Star-catalyzed oxidation of sec-alcohols was done according to the following procedures.[12a] K_2CO_3 (1 mmol, 138 mg) was placed in a baked 50 mL round-bottomed flask equipped with a condenser and three-way stopcock, and purged by dry argon. The solution of **C2** (0.01 mmol of core-Ru(II), 0.27g) in acetone (10 mL) and 1-phenylethanol (**S1**: 10 mmol, 1.21 mL) were added into the flask at 25 ^{o}C under dry argon. The reaction mixture was

stirred and refluxed at 65 ^{o}C and sampled in pre-determined period. The yield was determined by ^{1}H NMR analysis of the reaction solution.

Result and Discussion

1. Synthesis of Ru(II)-Bearing Polymer Catalysts

Ru(II)-bearing microgel star polymers with PMMA arms [Ru(II)-Star (**C1**-**C7**)] were employed as catalysts for oxidation of sec-alcohols via hydrogen transfer reaction, in comparison to Ru(II)-bearing polystyrene gel [Ru(II)-Gel (**C8**)], Ru(II)-bearing random copolymers [Ru(II)-Random (**C9**)], and original Ru(II) [$RuCl_2(PPh_3)_3$ (**C10**)]. The star polymer catalysts (**C1**-**C7**) were synthesized, in high yield (~90%), by $RuCl_2(PPh_3)_3$-catalyzed living radical polymerization of MMA with a chloride initiator, followed by the arm-linking reaction with a divinyl compound (**1**) and a phosphine-ligand monomer (**2**) (Scheme 1).[12a,12b] Here, the structure factors of the star polymers (**C1**-**C7**) were systematically varied in terms of the arm length (DP = [MMA]/[initiator] = 50 - 200), the amount of a linking agent (**1**) to initiator (r_1 = [**1**]/[initiator] = 5 - 20), the amount of an additional MMA into the core (r_{MMA} = $[MMA]_{core}$/[initiator] = 10), in addition to the amount of a ligand monomer (**2**) to initiator (r_2 = [**2**]/[initiator] = 1.25, 2.5). Table 1 summarizes the characterization data of the polymers by multi-angle laser light scattering coupled with size-exclusion chromatography (SEC-MALLS) and UV-vis. A gel catalyst (**C8**) was prepared by the immobilization of $RuCl_2(PPh_3)_3$ on a phosphine-bearing polystyrene gel (**3**). **C8** corresponds to a cut-out model of the microgel core of star polymer catalysts, however **C8** is insoluble in any solvent. A linear polymer catalyst (**C9**) is prepared by free radical random copolymerization of MMA and **2**, followed by the immobilization of $RuCl_2(PPh_3)_3$. The polymer

has the same composition of MMA and **2** as the core of **C2**, thus regarded as a linear analogue of the catalytic site of **C2**.

Table 1

2. Oxidation of Alcohols by Hydrogen Transfer Reaction

Effects of Catalyst Structure

Effects of polymer structures on the catalytic activity in oxidation of sec-alcohols was first investigated with Ru(II)-Star (**C2**: *DP* = 100, r_1 =10, r_2 = 2.5), Ru(II)-Gel (**C8**), Ru(II)-Random (**C9**), and the original Ru(II) [$RuCl_2(PPh_3)_3$ (**C10**)] (Figure1). Their polymer-supported catalysts were applied to the oxidation of 1-phenylethanol (**S1**) coupled with K_2CO_3 (base) in acetone (solvent; hydrogen accepter) at 65 ^oC (reflux) (Figure 1).[12a,20a] The feed molar ratio of a ruthenium catalyst to a substrate (**S1**) was set in [Ru(II)]/[**S1**] = 1/1000. The star polymers (**C2**) efficiently and homogeneously catalyzed the reaction to give a corresponding ketone, acetophenone, in high yield (92%) at 8 h, though the reaction rate was smaller than **C10**. Ru(II)-Gel (**C8**) and Ru(II)-Random (**C9**) also brought about the oxidation heterogeneously and homogeneously, respectively. However, they gave lower yields of products (**C8**: 64%, **C9**: 52%) in 8 h than **C2**. The high activity of **C2** is probably due to the homogeneous reaction inducing efficient accessibility of the substrate and acetone (hydrogen acceptor) onto the ruthenium center, and the unique environment of ruthenium catalysts that was concentrated in the nano-sized microgel core.

Figure 1

Next, the effects of structure factors of star polymer catalysts (**C1**-**C6**) on the catalytic activity were examined in the oxidation of **S1**, focusing on arm length [*DP* = 50 (**C5**), 100 (**C2**), 200 (**C4**)], core cross-linking amount [r_1 = 5 (**C1**), 10 (**C2**), 20 (**C3**)], and core-void volume with

an additional core-bound MMA [r_{MMA} = 0 (**C2**), 10 (**C6**)] under the constant ligand feed ratio (r_2 = 2.5) (Figure 2A-2C). All of the polymers efficiently induced the oxidation in high yield (~90% in 8 h), and the activity was uniquely independent of the arm length, the core cross-linking amount, and the core-void volume. This is probably because the substrate would be accessible enough to the catalytic center even in the case of a long arm length (*DP* = 200) and highly cross-linked core (r_1 = 20). Paradoxically explaining, the cross-linked core, even consisting of the large amount of r_1 (**C3**), would have sufficient void spaces inside the nano networks cross-linked by **1**, in which substrates, products, and acetone (hydrogen acceptor) can diffuse smoothly for catalysis (Scheme 2). Additionally, the number ratio of core-bound phosphine (**2**) to core-bound Ru(II) [N_2/N_{Ru}] in **C1** - **C6** is almost 3 to 4, meaning almost all the ruthenium is supported by about 3 to 4 numbers of core-bound **2**. Since $RuCl_2(PPh_3)_3$ originally carries 3 number of triphenylphosphine ligands, the vacant site numbers on the core-bound metal center and the rigidity (mobility) of the core-bound ruthenium would be almost identical through **C1** - **C6**. This factor would also induce the similar activity in the catalysis. Therefore, the star-shaped structure consisting of soluble arms and microgel core encapsulating ruthenium catalysts is responsible for the high activity distinguished from the other type of polymer-supported Ru(II).

Figure 2

Catalyst Recycle

Another perspective of the star polymer catalyst is the increase of stability caused by the encapsulating effect inside the microgel core. Thus, the reusability of Ru(II)-Star (**C2**) was investigated in the oxidation of 1-phenylethanol (**S1**), compared to the original Ru(II) (**C10**) (Figure 3). The recycle procedure was according to three steps: (1) after the reaction, evaporation

of solvent (acetone) to leave the catalyst, base (K_2CO_3), and non-volatile organic compounds such as an obtained product and an substrate residue; (2) double washing by hexane to remove the non-volatiles; (3) reload of a substrate and a solvent for next run. The reuse procedure was examined under argon (inert) and air (Supporting information: Figure S1). The star polymers (**C2**) catalyzed the oxidation even in 2nd/3rd runs without obvious loss of activity under inert atmosphere recovery (Figure 3A). Surprisingly, such reuse was achieved via the catalyst recovery even under air procedure (Figure 3B). During the recycle processes, the washing solvent (hexane) for the catalysts showed colorless (transparent), which demonstrates that ruthenium complexes are steady supported by the microgel-core. Thus, the almost pure products were easily obtained from the simple precipitation of Ru(II)-Star catalysts into hexane. In contrast, the activity of the conventional Ru(II) (**C10**) was apparently decreased in 3rd cycle even under argon recovery (Figure 3C). Additionally, **C10** lost the catalytic activity through the recovery under air, which is probably due to decomposition caused by the low stability against oxygen (Figure 3D). These superior reusability and oxidation-resistance of star polymer catalysts most likely arise from the effective protection of ruthenium complexes enclosed by multiple phosphine ligands inside the tough cross-linked network.

Figure 3

Catalyst Stability

The structural stability of star polymer catalyst (**C2**) through the recycle experiments was examined with several analyses such as SEC, ^{1}H NMR, and UV-vis. The shape and position of SEC curves hardly changed between before use (Figure 4A) and after 3 runs (Figure 4B), which indicate that the star catalysts maintained original conformation through the recycle experiments

and a star-star coupling hardly occurred during the oxidation.[12d] ^{1}H NMR analysis of the star polymers supported no decomposition of the PMMA arms via the transesterification between methyl ester of PMMA arms and substrates (1-phenylethanol) (Figure 4C, 4D).[12d]

Figure 4

The tolerance of core-bound ruthenium through the recycle processes was also analyzed with UV-vis spectroscopy. Figure 5 showed the spectra of Ru(II)-Star (**C2**) and $RuCl_2(PPh_3)_3$ (**C10**) through various recycle processes: **C2** before use (A), **C2** after 3rd run [recovery procedure: under argon (B), under air (C)], **C10** before use (D), and **C10** after 1 st run (recovery procedure: under argon) (E). The star polymers (**C2**) before catalysis (Figure 5A) exhibited broad absorptions including three λ_{max} (~ 400, 481, and 728 nm), which is quite similar to **C10** (**C5**: Figure 5D). After the recycle experiments, the two absorptions around 481 and 728 nm disappeared and intensity of absorbance around 400 nm of λ_{max} was dramatically increased in both catalysts (Figure 5B, 5E). This is caused by the transformation of the chloride complex into the hydride one through the oxidation reaction, which also confirmed by the color change from red-orange to yellow-orange. The **C2** through the recovery procedure under air also showed same absorption pattern (Figure 5C) as the above patterns (Figure 5B, 5E), meaning no decomposition of core-bound Ru(II) after air exposure. Actually, the star catalyst (**C2**) recovered under air still exhibited the identical yellow-orange color during recycle experiments, in sharp contrast to **C10** turning into black-brown under same condition. These results support that the core-bound Ru(II) of **C2** had high oxidation resistance to maintain the catalytic activity even if **C2** was recovered under air.

Figure 5

Various Substrates

Catalysis with Ru(II)-star polymers proceeds in the ruthenium-bearing microgel core surrounded by plenty of PMMA arms. Such a specific reaction field might induces different substrate selectivity from conventional $RuCl_2(PPh_3)_3$. Thus, we examined the oxidation of various sec-alcohols (**S1**~**S7**) with a star polymer catalyst (**C7**). The loaded molar ratio of a ruthenium catalyst to a substrate was set in [Ru(II)]/[substrate] = 1/1000. As shown in Table 2, **C7** catalyzed the oxidation of all substrates (**S1**~**S7**) to the corresponding ketones. The substrates containing aromatic groups (**S1**~**S3**) were efficiently oxidized to alcohol products in high yield (over 90% in 3 h) with appropriate turn over frequency (TOF > 300 h^{-1}). However, **C7** especially induced the slower oxidation of long alkyl sec-alcohol (**S7**) to give low TOF (57% Yield in 16 h, TOF = 37 h^{-1}).

Table 2

Finally, the substrate selectivity of Ru(II)-Star (**C7**) was compared with $RuCl_2(PPh_3)_3$ (**C10**). The selectivity was evaluated by the relative rate for each substrate to **S7** as a standard substrate on the basis of the reaction time to achieve 50% yield (half life period of substrate: $T_{1/2}$), where Relative rate ($K_{S7} = T_{1/2}$ (**S7**)/$T_{1/2}$) was used as an evaluation index (Figure 6). This is due to that **S7** gave the slowest oxidation with both catalysts among all substrates (time-yield curves obtained with **C7** and **C10** were listed in supporting information: Figure S2, S3). As seen in the Figure 6, the rates for aromatic compounds (**S1**~**S3**) tended to be larger than non-aromatic counterparts (**S4**~**S7**) with both catalysts. Specifically, the Ru(II)-Star (**C7**) gave much higher K_{S7} than **C10** for chlorine-substituted aromatic substrate (**S2**) and indane-substituted (**S3**). Such specific selectivity would be caused by the unique structural features of star polymer catalyst, such as the condensed catalysts and the confined reaction space around them. These results suggest the

challenging possibilities that star polymer catalysts should provide particular reaction pockets built by a more sophisticated design depending on substrates.

Figure 6

Conclusion

We have demonstrated that ruthenium-bearing microgel core star polymers with poly(MMA) arms, directly prepared by ruthenium-catalyzed living radical polymerization, efficiently and homogeneously catalyzed the oxidation of 1-phenylethanol (**S1**) in high yield (over 90%), in spite of low molar ratio of a ruthenium catalyst to the substrate ($[\mathbf{S1}]_0/[\mathrm{Ru(II)}]_0 = 1000/1$). They showed higher activity than the analogical catalysts supported onto linear random polymer or insoluble polystyrene gel. Recycle experiments with the star catalysts were achieved for three times without loss of activity even though they were recovered under air. The excellent stability of star polymer catalysts was also confirmed by the following spectroscopic characterization: SEC; ^{1}H NMR; and UV-vis. Furthermore, they exhibited substrate selectivity different from the conventional $RuCl_2(PPh_3)_3$. These features were derived from the unique structure consisting of cross-linked microgel core encapsulating ruthenium complexes and the covering soluble poly(MMA)-arms.

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Table 1. Characterization of Ru(II)-Bearing Star Polymer Catalysts [Ru(II)-Star][a]

Code	DP^a	$r_1{}^a$	$r_2{}^a$	$r_{MMA}{}^a$	$M_{w,\,star}{}^b$ (g/mol)	f^c (No.of Arms)	$N_2{}^d$ (No. of **2**)	Ru^e (μmol/g)	$N_{Ru}{}^f$ (No. of Ru)	$N_2/N_{Ru}{}^g$
C1	100	5	2.5	0	170,000	11	28	48	8.2	3.4
C2	100	10	2.5	0	388,000	24	60	38	15	4.1
C3	100	20	2.5	0	1,015,000	56	140	39	40	3.5
C4	200	10	2.5	0	824,000	27	68	22	18	3.7
C5	50	10	2.5	0	394,000	32	80	73	29	2.8
C6	100	10	2.5	10	412,000	24	60	35	14	4.2
C7	100	10	1.25	0	369,000	22	28	31	11	2.5

[a] Ru(II)-Star catalysts were prepared by $(MMA)_2$-Cl (initiator)/$RuCl_2(PPh_3)_3$/*n*-Bu_3N (additive)-mediated living radical polymerization of methyl methacrylate (MMA) in conjunction with ethylene glycol dimethacrylate (**1**) and diphenylphosphinostyrene (**2**) in toluene at 80 °C: DP = $[MMA]_0/[initiator]_0$ = 100; r_1 = $[\mathbf{1}]_0/[initiator]_0$; r_2 = $[\mathbf{2}]_0/[initiator]_0$; r_{MMA} = $[MMA]_{core}/[initiator]_0$.

[b] Absolute weight average molecular weight of star polymers determined by multi-angle laser light scattering coupled with SEC (SEC-MALLS)

[c] The number of core-bound **2** in a single star polymer molecule: $N_2 = r_2 \times f$.

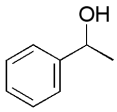
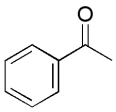
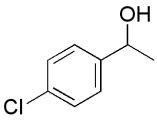
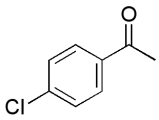
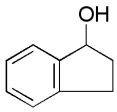
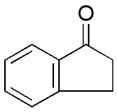
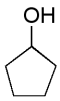
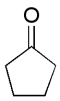
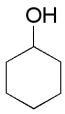
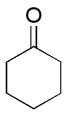
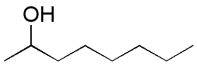
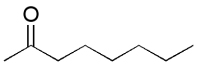
[d] The number of arms per a single star polymer molecule: f = (weight fraction of MMA) x $M_{w,star}/M_{w,arm}$ (SEC); $M_{w,arm}$ (SEC) = 12,900 (**C1**, **C3**, **C7**), 11,400 (**C2**, **C6**); 26400 (**C4**); 7,200 (**C5**); $M_w/M_{n,arm}$ (SEC) <1.25.

[e] The amounts of core-bound Ru(II) determined by UV-vis analysis.

[f] The number of Ru complexes per a single star polymer molecule: N_{Ru} = Ru (mol/g) x $M_{w,\,star}$ (g/mol).

[g] The ratio of core-bound **2** to core-bound Ru(II).

Table 2. Oxidation of sec-Alcohols Catalyzed by Ru(II)-Star (C7)[a]

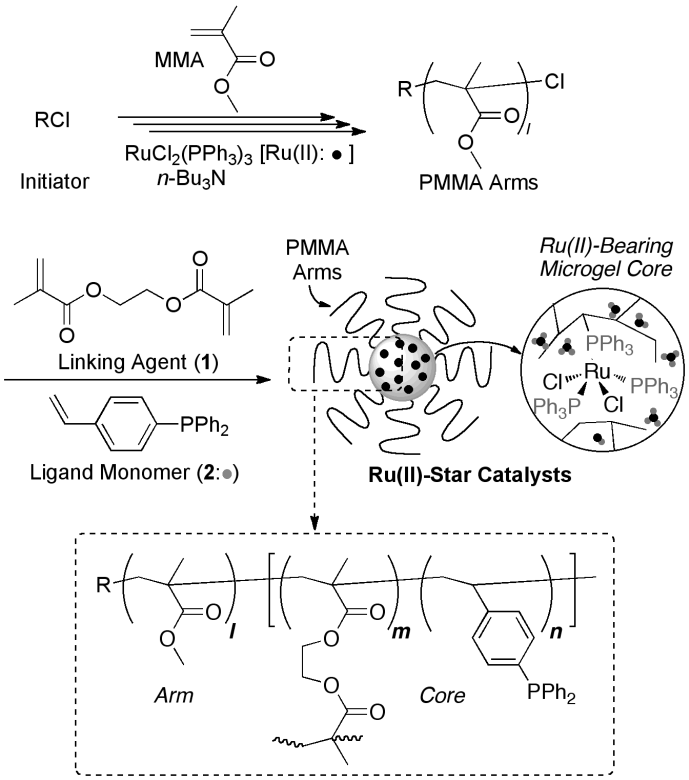
Code	Substrate	Product	*t* (h)	Yield[b] (%)	TOF[c] (h^{-1})
S1			3	90	300
S2			3	91	303
S3			3	96	320
S4			8	86	108
S5			10	60	60
S6			10	63	63
S7			16	57	37

[a] Substrate/**C7**-bound Ru(II)/K_2CO_3 = 10/0.010/1.0 mmol in acetone (10 mL) at 65°C.

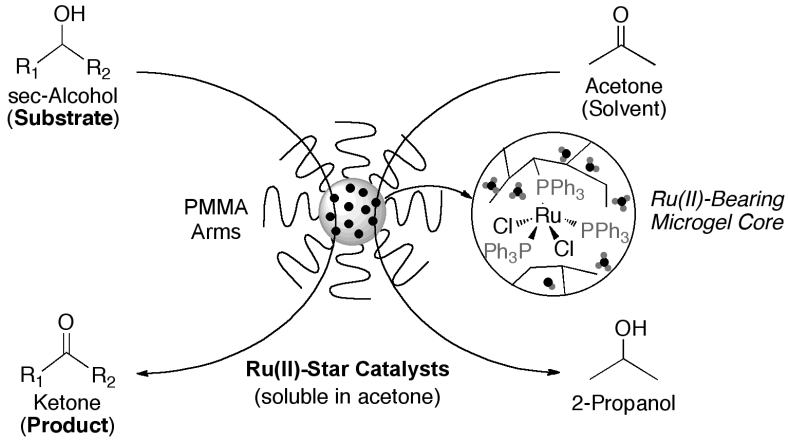
[b] Yields of products were determined by ^{1}H NMR.

[c] Turn over frequency: [Product]/([Ru(II)]$_0$ × *t*).

Schemes and Figures



Scheme 1. Synthesis of Ru(II)-Bearing Microgel Star Polymer Catalysts via Ru(II)-Catalyzed Living Radical Polymerization



Scheme 2. Oxidation of sec-Alcohols with Ru(II)-Bearing Microgel Star Polymer Catalysts [Ru(II)-Star Catalysts] in Acetone via Hydrogen Transfer Reaction

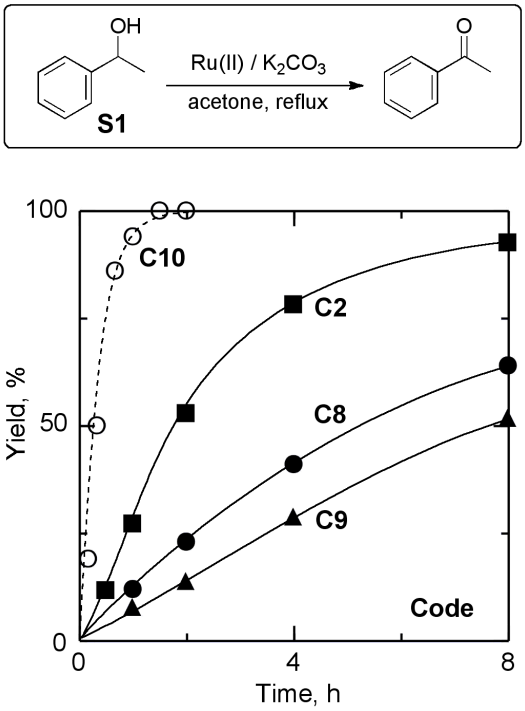


Figure 1. Effects of catalyst structure on oxidation of 1-phenylethanol (**S1**) with Ru(II)-Star (**C2**), Ru(II)-Gel (**C8**), Ru(II)-Random (**C9**), $RuCl_2(PPh_3)_3$ (**C10**): **S1**/Ru(II)/K_2CO_3 = 10/0.010/1.0 mmol in acetone (10 mL) at 65 °C.

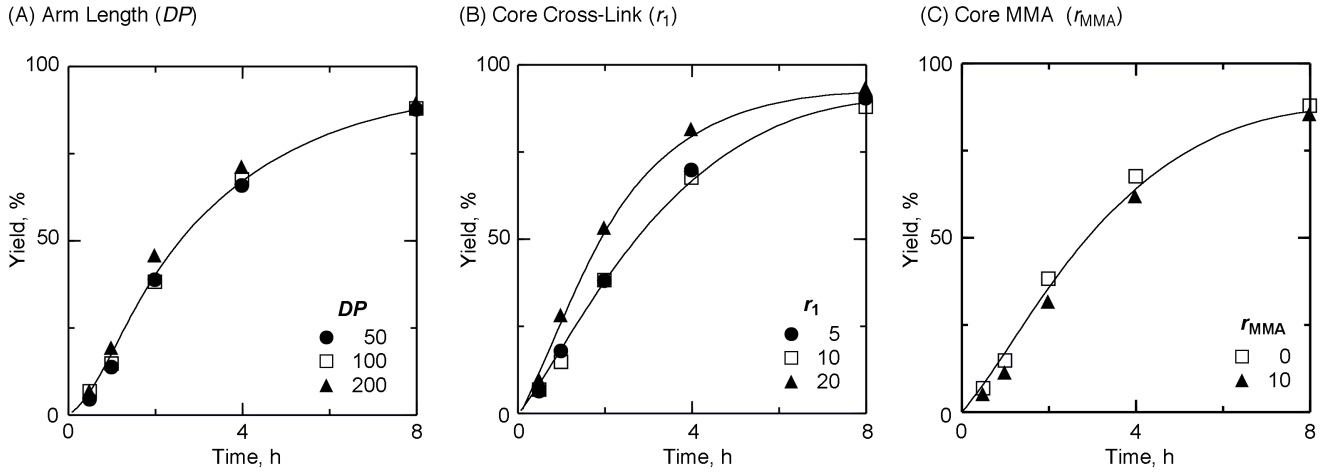


Figure 2. Effects of the arm length [A: *DP* = 50 (**C5**), 100 (**C2**), 200 (**C4**); r_1 = 10; r_2 = 2.5], the core cross-linking [B: *DP* = 100; r_1 = 5 (**C1**), 10 (**C2**), 20 (**C3**); r_2 = 2.5], and the core MMA [C: *DP* = 100; r_1 = 10; r_2 = 2.5; r_{MMA} = 0 (**C2**), 10 (**C6**)] of Ru(II)-Star on oxidation of 1-phenylethanol (**S1**): **S1**/Ru(II)/K_2CO_3 = 10/0.010/1.0 mmol in acetone (10 mL) at 65 °C.

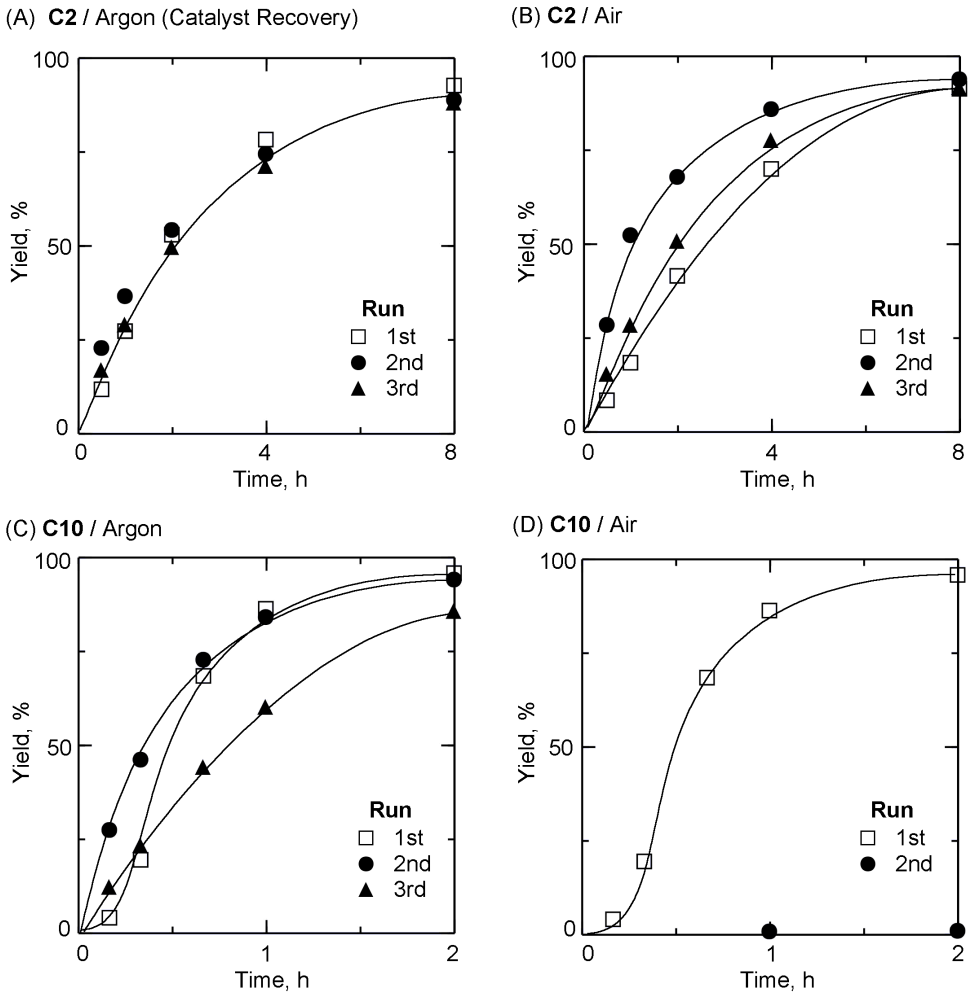


Figure 3. Recycle of Ru(II)-Star (**C2**) and $RuCl_2(PPh_3)_3$ (**C10**) in oxidation of 1-phenylethanol (**S1**): **S1**/Ru(II)/K_2CO_3 = 12/0.012/1.2 mmol in acetone (12 mL) at 65 ^oC.

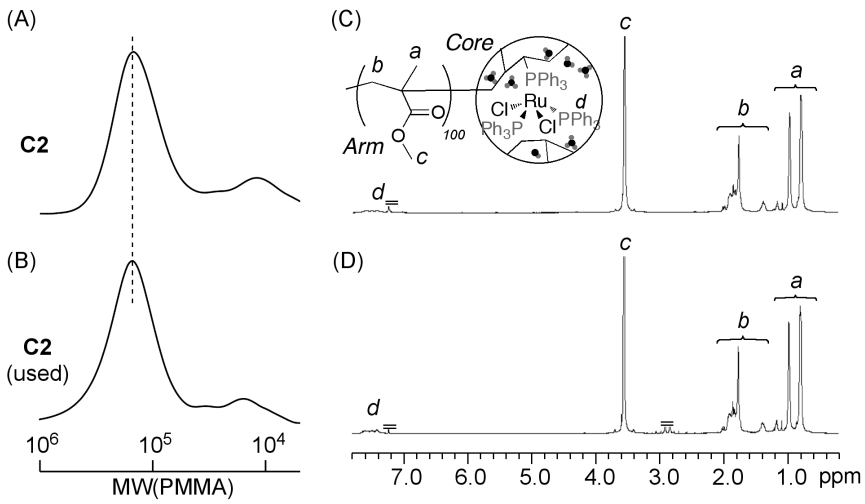


Figure 4. SEC curves (A, B) and ^{1}H NMR spectra (C, D: in $CDCl_3$ at 25 ^{o}C) of Ru(II)-Star (**C2**) employed for recycle experiment in oxidation of 1-phenylethanol (**S1**): (A, C) **C2** before use; (B, D) **C2** after 3 runs of the catalysis (Figure 3B 3rd).

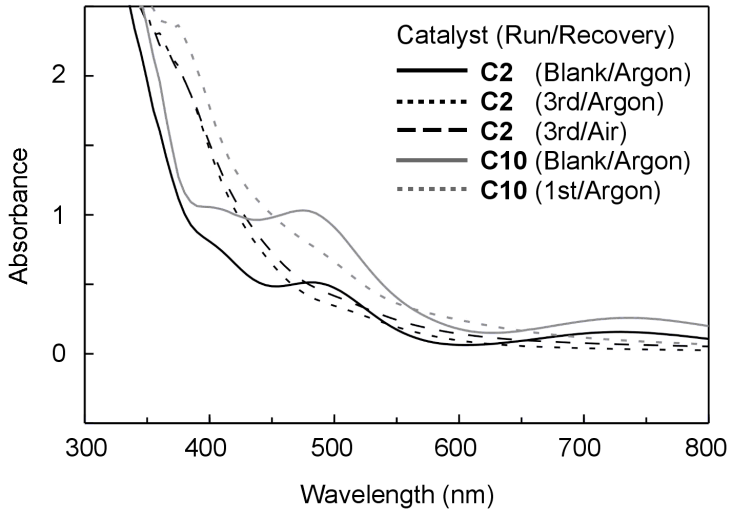


Figure 5. UV-vis spectra (in CH_2ClCH_2Cl at 25 ^{o}C) of Ru(II)-Star (**C2**) and $RuCl_2(PPh_3)_3$ (**C10**) employed for the recycle experiment in oxidation of 1-phenylethanol (**S1**): **C2** before use (black); **C2** after 3 rd run treated under argon (black dash); **C2** after 3 rd run treated under air (black long dash); **C10** before use (gray: 0.98 mM); **C10** after 1 st run trated under argon (gray dash: 1.2 mM); [**C1**] = 1.25×10^{-2} g/mL.

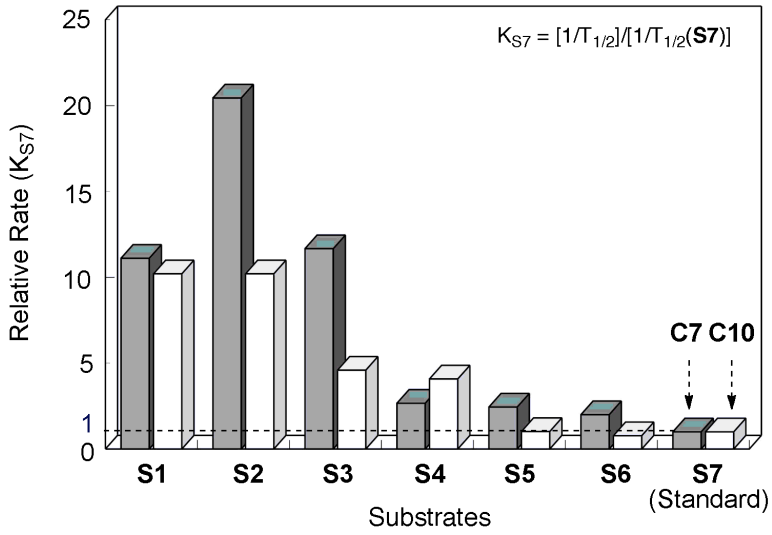
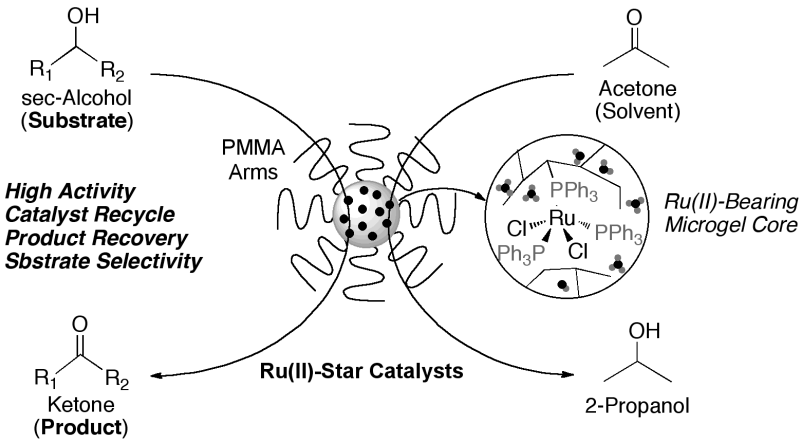


Figure 6. Relative rates (K_{S7}) calculated from the half life period ($T_{1/2}$) of substrates in comparison to that of 2-octanol (**S7**: standard) in Ru(II)-Star (**C7**) or $RuCl_2(PPh_3)_3$ (**C10**)-catalyzed oxidation. Relative rate: $K_{S7} = T_{1/2}(\mathbf{S7})/T_{1/2}$. Conditions: substrate/Ru(II)/K_2CO_3 = 10/0.010/1.0 mmol in acetone (10 mL) at 65°C.

Graphical Abstract

Oxidation of sec-Alcohols with Ru(II)-Bearing Microgel Star Polymer Catalysts via Hydrogen Transfer Reaction: Unique Microgel-Core Catalysis

Takaya Terashima,[1)]* Makoto Ouchi,[1)] Tsuyoshi Ando,[1)2)] Mitsuo Sawamoto[1)]*



Oxidation of sec-alcohols was investigated with ruthenium-bearing microgel core star polymer catalysts [Ru(II)-Star]. Ru(II)-Star efficiently and homogeneously catalyzed the oxidation of 1-phenylethanol (**S1**) to give a corresponding ketone (acetophenone) in higher yield (92%) than analogues of polymer-supported ruthenium complexes. Importantly, the star catalysts afforded high recycling efficiency against the three times catalysis even via the catalyst recovery under air-exposure, while the conventional $RuCl_2(PPh_3)_3$ lost the activity for same recycling procedure. Furthermore, the star polymer catalysts showed unique selectivity different from $RuCl_2(PPh_3)_3$.